

# Determination of the density of localized states in semiconductors from the pre-recombination transient photoconductivity

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Received 6 December 2006; received in revised form 1 July 2007; accepted 17 July 2007

Available online 31 August 2007

The review of this paper was arranged by Prof. Y. Arakawa

## Abstract

In this paper we present a new transient photoconductivity (TPC) inversion method for the determination of the density of localized states (DOS) energy distribution  $g(E)$  in thin film semiconductor materials with exact matrix solution for  $g(E)$ . The method, derived from the multiple trapping model, is based on prior determination of the exact transient trap occupation function and applies to the pre-recombination time range of the TPC. It is demonstrated by application to simulated TPC data that high energy resolution can be achieved for the case of continuous DOS distribution, appropriate to amorphous semiconductors, as well as for discrete level DOS such as in crystalline semiconductors.

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**Keywords:** Amorphous semiconductors; Photoconductivity; DOS; Pre-recombination; Occupation function

## 1. Introduction

Information on localized states distribution in both amorphous and crystalline semiconductors is important for the understanding of their fundamental electronic properties. Since the TPC in thin film semiconductors is strongly influenced by the energetic distribution of localized states in the band gap, several spectroscopy techniques for the DOS extraction from the TPC have been developed [1–10]. The continuous distribution of localized states results in simultaneous interactions of excess free carriers with a wide range of these states. If an excess carrier density is created by means of a short light pulse in samples with coplanar electrode configuration, the subsequent TPC decay contains useful information on the DOS distribution in the material. Unfortunately, most of the techniques can only detect indirectly the DOS.

A series of projects have been devoted to the investigation of the relationship between the DOS  $g(E)$  and the number of excess free carriers  $n(t)$  that is often obtained from transient photocurrent experiments.

A first spectroscopic interpretation of multiple trapping transport in amorphous semiconductors was offered by Tiedje and Rose [11], and independently by Orenstein and Kastner [12] (this work as a whole is sometimes referred to a TROK). It requires a continuous and suitable broad (e.g., exponential) band tail and the absence of carrier losses by recombination or completion of transit. Thermalization is envisaged as occurring such that, at time  $t$  after optical excitation of  $N_0$  excess carriers, most of these are concentrated in states close (within an energy range  $kT$ ) to a “thermalization energy”,  $E_{th}$ . This is defined as the depth at which states have a release time constant equal to the elapsed time:  $E_{th} = kT \ln(\nu t)$ , where  $\nu$  is the attempt-to-escape frequency for the localized states,  $T$  is the temperature, and  $k$  is Boltzmann’s constant. All energy values are measured downwards from the conduction band mobility edge,  $E_c$ .

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With various approximations, this model yields a density of localized states at energy  $E_{\text{th}}$  of the form  $N(E_{\text{th}}) = \frac{C}{n(t)^{\alpha}}$ , where the constant  $C = \frac{N_0 N(E_c)}{\nu}$ , with  $N(E_c)$  being the effective density of states at the mobility edge.

Later, a general approximate relation between  $g(E)$  and  $n(t)$  has been established by Michiel, Adriaenssens and Marshall [13]. In their approach, the DOS is linked to the transient photocurrent via a Volterra integral equation of the first kind, the solution of which requires the use of complex numerical methods.

We develop in this article a new method that improves our previous work [14] to extract the DOS distribution without approximations by a direct inversion of the pre-recombination TPC. In contrast to existing Fourier and Laplace transform related techniques [4,7], the inversion is performed here in the time domain. The method uses the exact transient trap occupation function calculated with accuracy from the TPC. It is shown that this transient spectroscopy reconstructs pre-proposed arbitrary DOS models from the associated simulated TPC with high energy resolution and without the influence associated with the temperature broadening of the carrier distribution.

## 2. Transient trap occupation function

The transient occupation function of localized states in amorphous semiconductors was calculated by Benyuan and Zhengyi from a recombination free transient photocurrent of a power-law time variation,  $n(t) = At^{-(1-\alpha)}$ , that is usually observed in undoped a-Si:H and a-As<sub>2</sub>Se<sub>3</sub> materials [15]. The authors used this transient trap occupation function to derive a relationship between the DOS  $g(E)$  and the density of excess free carriers  $n(t)$  in the form of a Volterra integral equation of the second kind [16]. By solving this equation, they have shown that the DOS is expressed by a single exponential function with a steepness characteristic temperature  $T_0 = \frac{T}{\alpha}$  extending over a wide energy range below  $E_c$ .

In the present work, the transient trap occupation function is calculated more rigorously from the pre-recombination TPC data simulated using a rather arbitrary DOS distribution. We consider that the transport is due to electrons in extended states. The excess free carriers can be repeatedly trapped and released from the localized states. Thus the photocurrent response is governed by the following equations, for the free  $n(t)$  and the trapped  $n_t(E, t)$  electron densities, respectively,

$$n(t) = N_0 - \int_{E_f}^{E_c} g(E)[1 - f(E)]f_t(E, t)dE, \quad (1)$$

$$\frac{\partial n_t(E, t)}{\partial t} = -v(E)n_t(E, t) + C_n n(t)[g(E)dE - n_t(E, t)]. \quad (2)$$

$N_0$  is the pulsed electron density, the excess free electron density at the initial time  $t = 0$ .  $v(E)$  is the mean release rate from a trap at energy  $E$ , given by

$$v(E) = v_0 \exp\left(\frac{E}{kT}\right) \quad \text{for } E \leq 0,$$

where  $v_0$  is the attempt-to-escape frequency of the release process related to the capture coefficient  $C_n$  via  $v_0 = N(E_c)C_n$ . We set the conduction band mobility edge at  $E_c = 0$ , so that  $E$  is negative. The integral in Eq. (1) expresses the excess-trapped charge. The thermal equilibrium occupied DOS  $g(E)f(E)$  is subtracted from the total DOS  $g(E)$ , since only the empty states intervene in the excess carrier capture, where

$$f(E) = \left[1 + \exp\left(\frac{E - E_f}{kT}\right)\right]^{-1} \quad (3)$$

is the Fermi distribution, with  $E_f$  the dark Fermi level. The transient trap occupation function  $f_t(E, t)$  is then related to  $n_t(E, t)$  by

$$n_t(E, t) = g(E)[1 - f(E)]f_t(E, t)dE. \quad (4)$$

Inserting Eq. (4) into Eq. (2), the rate equation controlling the transient trap occupation function is

$$\frac{\partial f_t(E, t)}{\partial t} + [C_n n(t) + v(E)]f_t(E, t) = \frac{C_n n(t)}{1 - f(E)}, \quad (5)$$

with  $f_t(E, 0) = 0$  for  $E > E_f$ .

$f_t(E, 0)$  denotes the thermal equilibrium occupation function for the trapping states before photoexcitation.

For any  $n(t)$ , the solution of Eq. (5) after discretisation can be expressed as a matrix element

$$f_t(E_i, t_j) = \frac{f_t(E_i, t_{j-1}) + \frac{C_n n(t_j)(t_j - t_{j-1})}{1 - f(E_i)}}{1 + [C_n n(t_j) + v(E_i)](t_j - t_{j-1})}$$

for  $i = 1, \dots, M$   
 $j = 2, \dots, N$ , (6)

with  $f_t(E_i, t_1) = 0$  for  $i = 1, \dots, M$ , the initial condition and where  $M$  and  $N$  are, respectively, the number of discrete levels between  $E_c$  and  $E_f$  and the number of data time points. Fig. 1c shows the time-dependent energy distribution of the calculated  $f_t(E, t)$  (symbol o) at 350 K for an exponential distribution of localized states  $g(E) = g(E_c) \exp(\frac{E}{kT_c})$ , where  $g(E_c) = 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$  and  $T_c = 300 \text{ K}$  (Fig. 1a) using the simulated TPC curve shown in Fig. 1b based on a finite difference technique [17,18]. The occupation function deduced from the simulation as the fraction  $\frac{n_t(E, t)}{g(E)[1 - f(E)]dE}$  is also presented in Fig. 1c (solid line). The calculated and simulated curves  $f_t(E, t)$  are completely superimposed.

The previous work [14] consisted of the determination of the transient occupation function  $f_t(E, t)$  from a transient photocurrent  $n(t)$  and consequently the determination of the density of localized states  $g(E)$ . This transient occupation function was postulated by Schiff [19] as  $f_t(E, t) = \frac{F(t)}{1 + \exp(\frac{E - E_t}{kT})}$  where  $E_t = -kT \ln(v_0 t)$  and  $F(t) = C_n n(t)$ . For energy levels deeper than  $E_t$ ,  $f_t(E, t)$  reduces to  $F(t)$ , assumed to be independent of energy. It is only an approximation and is only valid for an exponen-

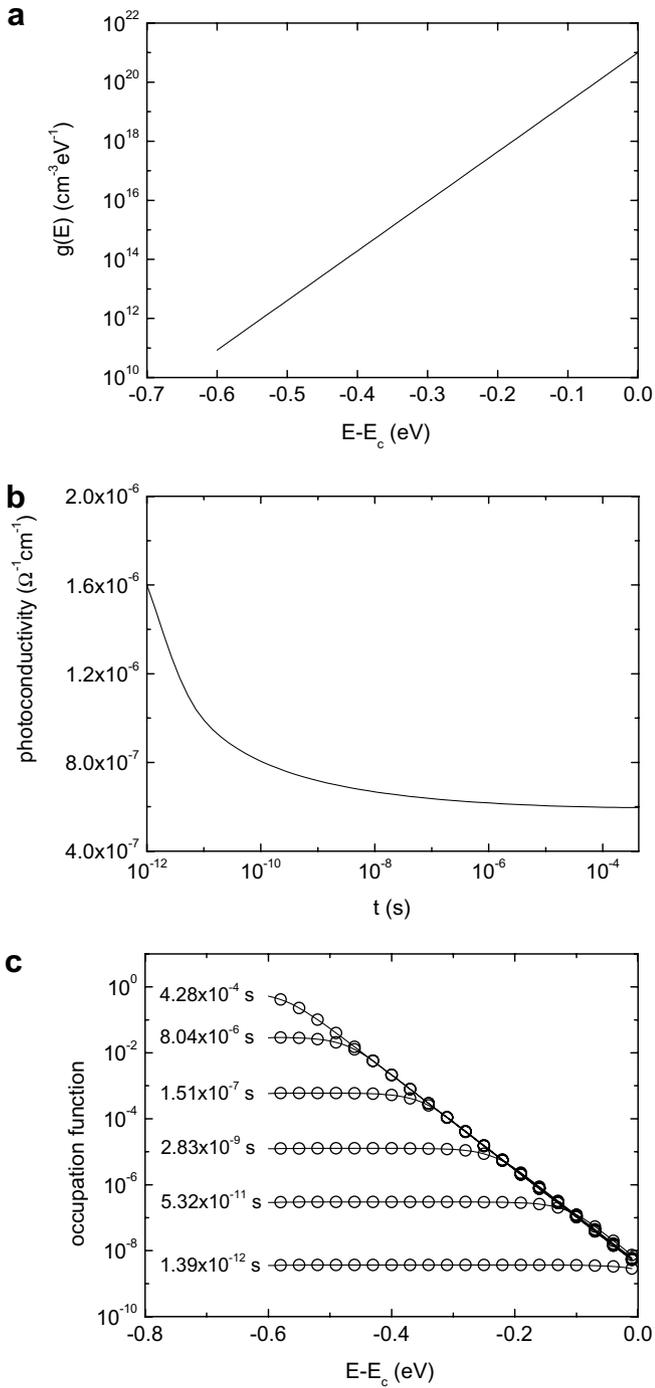


Fig. 1. (a) Exponential DOS model with characteristic temperature  $T_c = 300$  K. (b) Simulated TPC at 350 K for the DOS of (a). (c) Transient trap occupation function at six different times: calculated using Eq. (6) (symbol  $\circ$ ), and simulated as  $f_i(E, t) = \frac{n_i(E, t)}{g(E)[1-f(E)]dE}$  (solid line).

tial distribution of localized states and for a measurement temperature less than or equal to characteristic temperature  $T_c$ . For instance, Fig. 2 shows the time-dependent energy distribution of this transient occupation function (symbol  $\circ$ ) at 400 K for the density of localized states of Fig. 1a using the associated simulated photocurrent. The occupation function deduced from the simulation as the

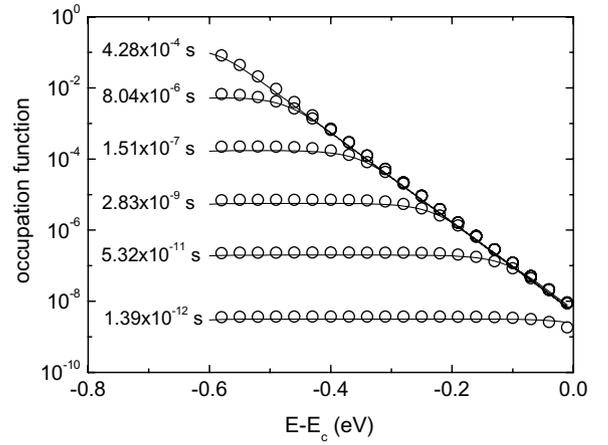


Fig. 2. Transient occupation function at six different times: postulated by Schiff (symbol  $\circ$ ), and simulated as  $f_i(E, t) = \frac{n_i(E, t)}{g(E)[1-f(E)]dE}$  (solid line).

fraction  $\frac{n_i(E, t)}{g(E)[1-f(E)]dE}$  is also presented (solid line). One can see that both curves are not completely superimposed.

### 3. Density of localized states $g(E)$

Written in a discrete form, Eq. (1) yields

$$b(j) = \sum_{i=1}^M N_t(i)A(j, i) \quad \text{for } j = 2, \dots, N, \quad (7)$$

where  $j$  and  $i$  are the time and energy indexes, respectively, and  $N_t(i) = g(E_i)dE_i \cdot g(E_i)$  is the density of states at the  $i$ th localized level below the mobility edge.  $dE_i$  is the spacing of the set of  $M$  discrete levels so that the energy at the  $i$ th level is  $E_i = E_c - (i - 1)dE_i$ . The vector elements  $b(j)$  and the matrix elements  $A(j, i)$  are, respectively,

$$b(j) = N_0 - n(j),$$

$$A(j, i) = \left[ 1 + \exp\left(\frac{E_f - E_i}{kT}\right) \right]^{-1} f_i(i, j),$$

where  $f_i(i, j)$  is obtained from Eq. (6).

The DOS vector is then given by

$$N_t = A^{-1}b. \quad (8)$$

This expression constitutes the basis of the pre-recombination transient method that returns for the occupation function  $f_i(i, j)$  (i.e., the TPC data) a DOS distribution  $g(E)$  of localized states. Eq. (8) is a Fredholm integral equation of the first kind which may arise from an ‘ill-conditioned problem’ and, consequently, needs a special resolution method. The resolution method used here is an exact matrix solution for  $g(E)$  based on Tikhonov regularization [20]. The basis of the method we used was developed by Hansen [21], but this method has been modified to give an iterative procedure.

### 4. Application to simulated TPC

To evaluate the proposed method, we compute  $n(t)$  for several representative distributions of traps. We then

calculate the density of states from the  $n(t)$  data using Eqs. (6) and (8) successively.

#### 4.1. Continuous DOS distribution

In Fig. 3, we show the reproduced  $g(E)$ , for three different temperatures, when the original distribution is an exponential tail  $g(E) = g(E_c) \exp\left(\frac{E}{kT_c}\right)$  with the characteristic temperature  $T_c = 300$  K. The temperatures used in the simulation are, respectively, 250, 300 and 350 K. It can be seen that the reconstructed DOS is an accurate representation of the original DOS independently of  $T$ .

In Fig. 4, we show the reproduced  $g(E)$  when the original distribution is an exponential distribution of characteristic temperature  $T_c = 300$  K to which the following Gaussian distribution is added:

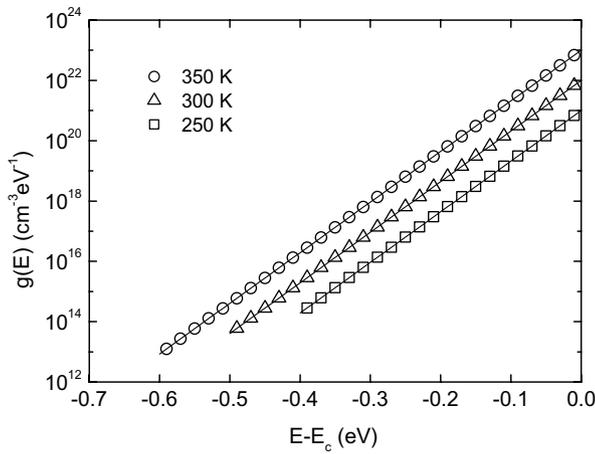


Fig. 3. Exponential DOS distribution with  $T_c = 300$  K, recovered from computed TPC,  $n(t)$ , at three different temperatures (symbols). The solid lines indicate the model DOS distribution. For clarity, the curves are multiplied by the factors 1, 10 and  $10^2$ , from bottom (250 K) to top (350 K).

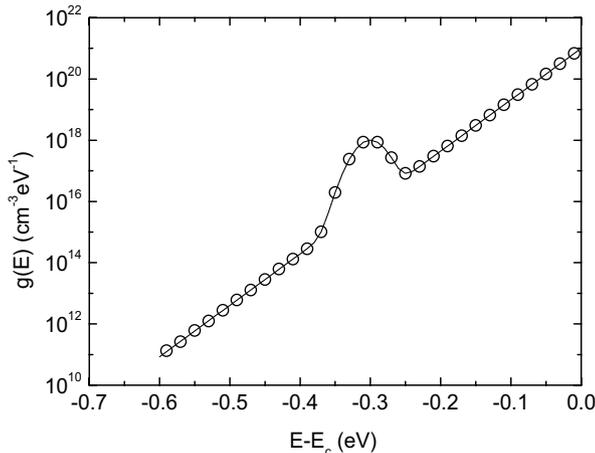


Fig. 4. Exponential plus Gaussian distribution of states with  $T_c = 300$  K,  $g_g = 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ ,  $E_g = -0.3$  eV and  $E_w = 25$  meV recovered from computed  $n(t)$  at 350 K (circles). The solid line indicates the model DOS distribution.

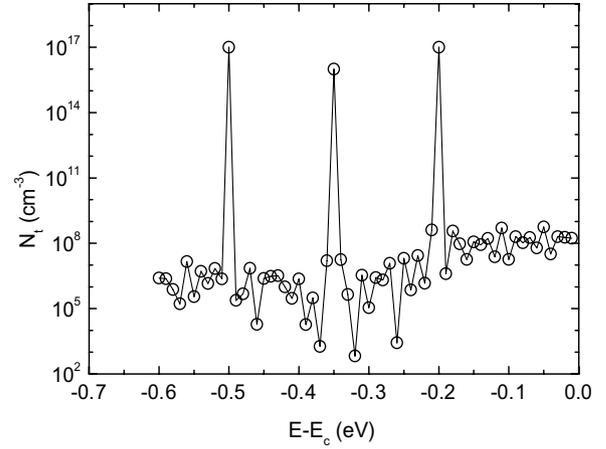


Fig. 5. Density of states recovered from computed  $n(t)$  at 350 K for two discrete levels at  $-0.2$  and  $-0.5$  eV depth, of density  $10^{17} \text{ cm}^{-3}$ , flanking a third discrete level at depth  $-0.35$  eV with a lower density  $10^{16} \text{ cm}^{-3}$ .

$$g(E) = g(E_c) \exp\left(\frac{E}{kT_c}\right) + g_g \exp\left[-\left(\frac{E - E_g}{E_w}\right)^2\right],$$

where  $g_g$ ,  $E_g$  and  $E_w$  are, respectively, the peak value, the energy position from the mobility edge and the energy width of the Gaussian distribution. The temperature used in the simulation is 350 K. It can be seen here also that the proposed method recovers very precisely the original DOS.

#### 4.2. Discrete level DOS

In Fig. 5, we test the method using two discrete levels of equal density  $10^{17} \text{ cm}^{-3}$ , at depths  $-0.2$  and  $-0.5$  eV, flanking a third discrete level of lower density  $10^{16} \text{ cm}^{-3}$ , at depth  $-0.35$  eV. The temperature used in the simulation is 350 K. We note that the discrete levels are represented now by broadened  $g(E)$  distributions, which when integrated should represent the same total density. It is clear that the method gives a fairly sharp reproduction of the discrete levels distribution, allowing ready identification of the centre level. The energy positions are recovered with high accuracy.

The following physical quantities appropriate to amorphous and crystalline semiconductors were used in the computation:  $N_0 = 10^{12} \text{ cm}^{-3}$ ,  $C_n = 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  and  $v_0 = 10^{12} \text{ s}^{-1}$ .

## 5. Conclusion

We have developed and examined a direct pre-recombination TPC inversion for determination of the localized states density distribution  $g(E)$  in semiconductors using accurate calculations by Tikhonov regularization method. High accuracy and energy resolution are noticeable. The method is based on a prior determination of the exact transient trap occupation function. It has been tested by applying it to simulated TPC data. It recovers precisely the

actual pre-proposed DOS in the cases of featured continuous or discrete distributions.

### Acknowledgement

The authors thank the Algerian Ministry of Higher Education and Research for financial support.

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